and 500 mL of benzene (distilled over sodium) were placed in an oven-dried 2-L three-neck round-bottom flask equipped with a 500 mL addition funnel, condenser, nitrogen inlet, and overhead stirrer. $TiCl_4$ (9.5 g, 5.5 mL, 0.05 mol) in 100 mL of benzene was added to the reaction mixture with stirring at 0 °C. The mixture was allowed to warm to room temperature over a 5-h period and then was heated at reflux. After several days, a white precipitate began to form. After a reaction period of 3 weeks, IR spectroscopy indicated the absence of carbonyl absorption. The mixture was cooled and filtered, and the solvent was removed. The residue was crystallized from hexane to yield 5.0 g of a tan solid: NMR ($CDCl_3$) δ 0.O7, 1.00, and 1.63 (s, 3 H each, CH_3), 1.71 (s, 9 H, $C(CH_3)_3$), 1.08–2.33 (m, 5 H, $-CH_2CH_2CH$), 2.56 (AB pattern, 1 H, J_{AB} = 19.5 Hz, 1 H, *endo*-HCHC=N), 3.16 (d of AB pattern, J_{AB} = 19.5 Hz, J = 6.0 Hz, 1 H, *exo*-HCHC=N); IR (KBr) 3180, 3040, 2800–3000, 1670, 1445, 1400, 1375, 1250, 1200, 950, 900, 780 cm^{-1}; MS (10 eV) *m/e* (relative intensity) 207 (56.4), 192 (58.5), 150 (44.2), 136 (22.9), 109 (100), 57 (94.8), 36 (30.9).

2-*tert*-Butyl-3-[(1*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-yl]oxaziridine (8). *m*-Chloroperoxybenzoic acid (607 mg, 3.0 mmol) in CH_2Cl_2 was added over 30 min to a solution of **7** (500 mg, 2.4 mmol) in CH_2Cl_2 at 0 °C. The mixture was stirred for 4 h at 0 °C, filtered, and extracted twice with 10% Na_2CO_3. The organic layer was dried (K_2CO_3), and the solvent was removed under vacuum to yield a yellow oil: NMR (CCl_4) δ 0.82, 0.07, and 0.91 (s, 3 H each, CH_3), 1.17 (s, 9 H, *t*-Bu), 1.1–2.5 (m, 7 H, $-CH_2CH_2CHCH_2-$); MS (70 eV) *m/e* (relative intensity) 223 (11.6), 208 (16.5), 167 (26.0), 150 (22.6), 57 (100), 41 (69.2), 29 (26.9).

Acknowledgment. This work was partially supported by grants from the National Science Foundation and the National Institutes of Health.

Registry No.—**1a,** 62107-41-9; **1b,** 63017-52-7; **1c,** 67425-86-9; **1d,** 67425-87-0; **1e,** 67425-88-1; **1f,** 63017-53-8; **1g,** 67504-37-4; **1h,** 67425-89-2; **1i,** 67425-90-5; **1j,** 63087-57-0; **1k,** 62058-74-6; **1l,** 59905-68-9; **1m,** 67504-72-7; **1n,** 67425-91-6; **1o,** 67462-99-1; **1p,** 67463-00-7; **1q,** 67463-01-8; **1r,** 67463-02-9; **1s,** 67425-83-6; **1t,** 67425-84-7; **1u,** 67462-98-0; **1v,** 67425-85-8; (*S*)-(+)-**2b,** 63017-54-9; (*S*)-(+)-**2c,** 59153-46-7; (*R*)-(−)-**2c,** 67425-97-2; **7,** 67425-95-0; **8,** 67425-96-1; **19,** 64954-02-5; **20,** 56907-09-6; **21,** 67425-92-7; **22,** 67425-93-8; **23,** 67425-94-9.

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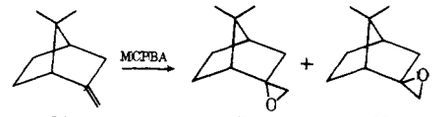

24 25 26

84%, endo 16%, exo

(9) Presumably, **1g** deviates from this behavior because the nonequivalence arises from differential isopropyl rotamer populations for the diastereomeric solvates and actually stems from internal magnetic anisotropy rather than from that of **2.** The magnitude of this type of nonequivalence is usually small relative to that having the usual origin. This phenomenon is most apt to occur for nonsymmetric rotors in molecules having nearby groups possessing substantial magnetic anisotropy.
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Quinazolines and 1,4-Benzodiazepines. 88.[1] Synthesis and Rearrangement of 3a,4,5,6-Tetrahydro-3*H*-imidazo[1,5-*a*][1,4]benzodiazepines

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The chemical and catalytic reduction of the dihydroimidazobenzodiazepine **2** afforded the *trans*-tetrahydroimidazobenzodiazepine **5** and the corresponding cis isomer **6,** respectively. Treatment of these reduced benzodiazepines with tosyl chloride resulted in cyclization to the two epimeric triazatricyclodecanes **7** and **9.** Thermolysis of these compounds led to the vinyl sulfones **13** and **14** involving an unusual 1,3 migration of the sulfonyl group. The structures of **14** and the *N*-nitroso derivative of **13** were determined by single-crystal X-ray analyses.

During the course of synthetic studies related to the preparation of 4*H*-imidazo[1,5-*a*][1,4]benzodiazepines,[2] the 2-aminomethylbenzodiazepine **1** was stereoselectively reduced with zinc and acetic acid to the corresponding tetrahydrobenzodiazepine **4,** which we designate as the trans isomer (Scheme I). Treatment of **4** with triethyl orthoacetate afforded the tetrahydroimidazobenzodiazepine **5** in which the hydrogens at C_2 and C_5 retain their trans stereochemistry. This same compound was also obtained by zinc and acetic acid reduction of the imine function in the dihydroimidazobenzodiazepine **2.**[2] Hydrogenation of **2** using platinum as catalyst gave exclusively the cis isomer, compound **6.** It has been shown[2] that

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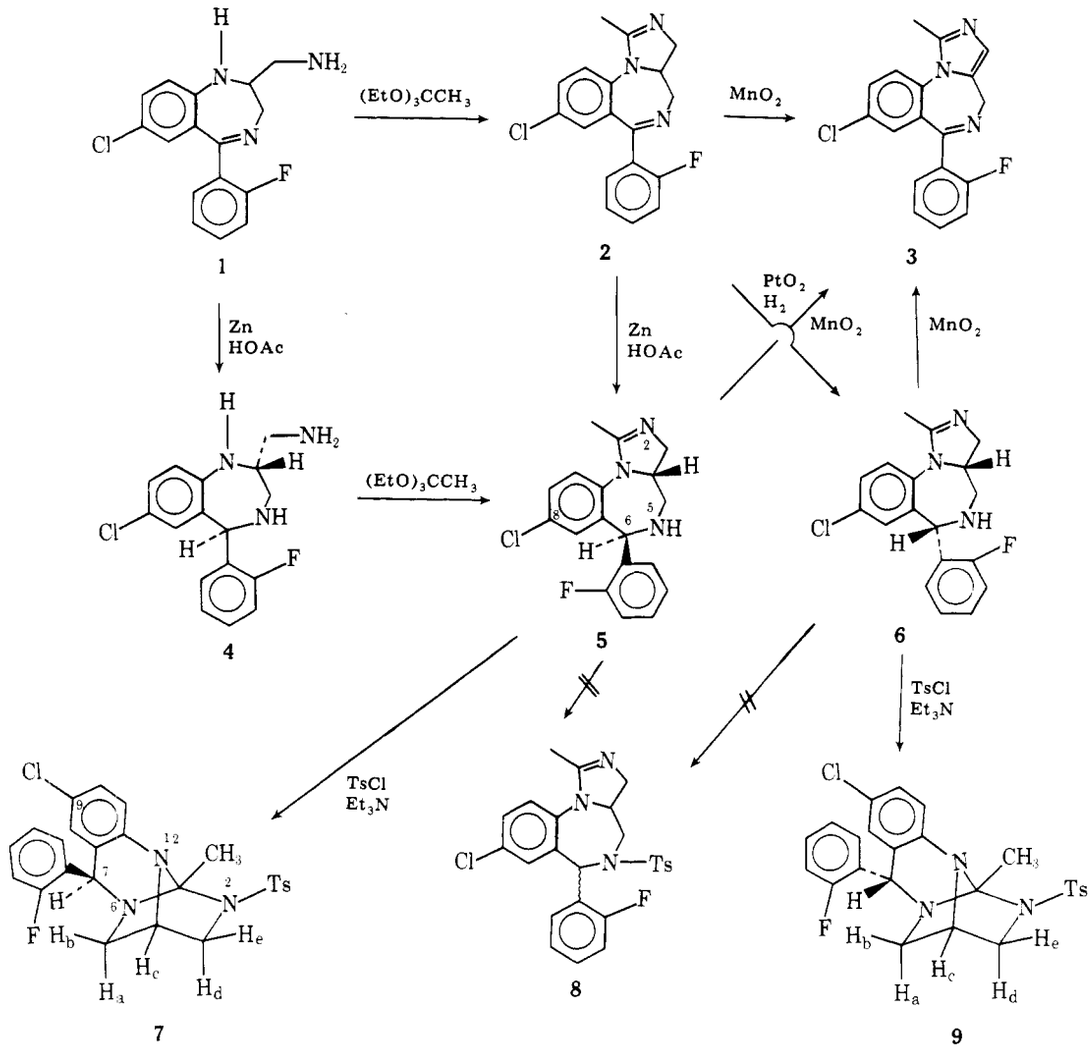
Scheme I



manganese dioxide oxidation of **2** gives the imidazobenzodiazepine **3**, and under the same conditions both isomers **5** and **6** were converted into compound **3**.

An attempt to form the 5-tosyl derivatives of **5** and **6** using tosyl chloride and triethylamine gave none of the expected sulfonamides **8**,[3] but only the tricyclic isomers **7** and **9**, respectively. The position of the tosyl group in both **7** and **9** was determined by the methanolysis of the orthoamide groups. Thus, refluxing methanol solutions of **7** and **9** gave the sulfonamides **11** and **12**, respectively. The structures of these compounds were confirmed by alternate syntheses. Thus, the amine **1** was converted to the sulfonamide **10** by reaction with tosyl chloride and triethylamine (Scheme II). Reduction of **10** with zinc and acetic acid led to **11** while hydrogenation of **10** using platinum oxide as catalyst yielded **12**.

The bridged orthoamide structure and the stereochemical orientation of the fluorophenyl group in both compounds **7** and **9** were assigned by inspection of their NMR spectra and by spin decoupling experiments. The NMR data of **7** and **9** are listed in Table I.

A long range coupling constant of 2 Hz was removed from the NMR signal of H_b in both **7** and **9** by direct irradiation of H_e. A similar simplification of the H_e NMR signal was observed by direct irradiation of H_b. This long range proton coupling indicates a coplanar relationship between protons H_b and H_e, which is consistent with the rigid norbornyl-type structures **7** and **9**[4] and not with the expected product **8**.

The stereochemistry of the fluorophenyl group can be deduced from the NMR spectra of **7** and **9**. The chemical shift of proton H_a in isomer **7** is 0.90 ppm, which is 0.91 ppm upfield of the proton H_a in **9**. This indicates that the fluorophenyl group in **7** shields proton H_a. Conversely, the chemical shift of the methyl protons in the exo isomer **9** is 1.56 ppm, which is 0.45 ppm upfield of the methyl group protons in **7**.

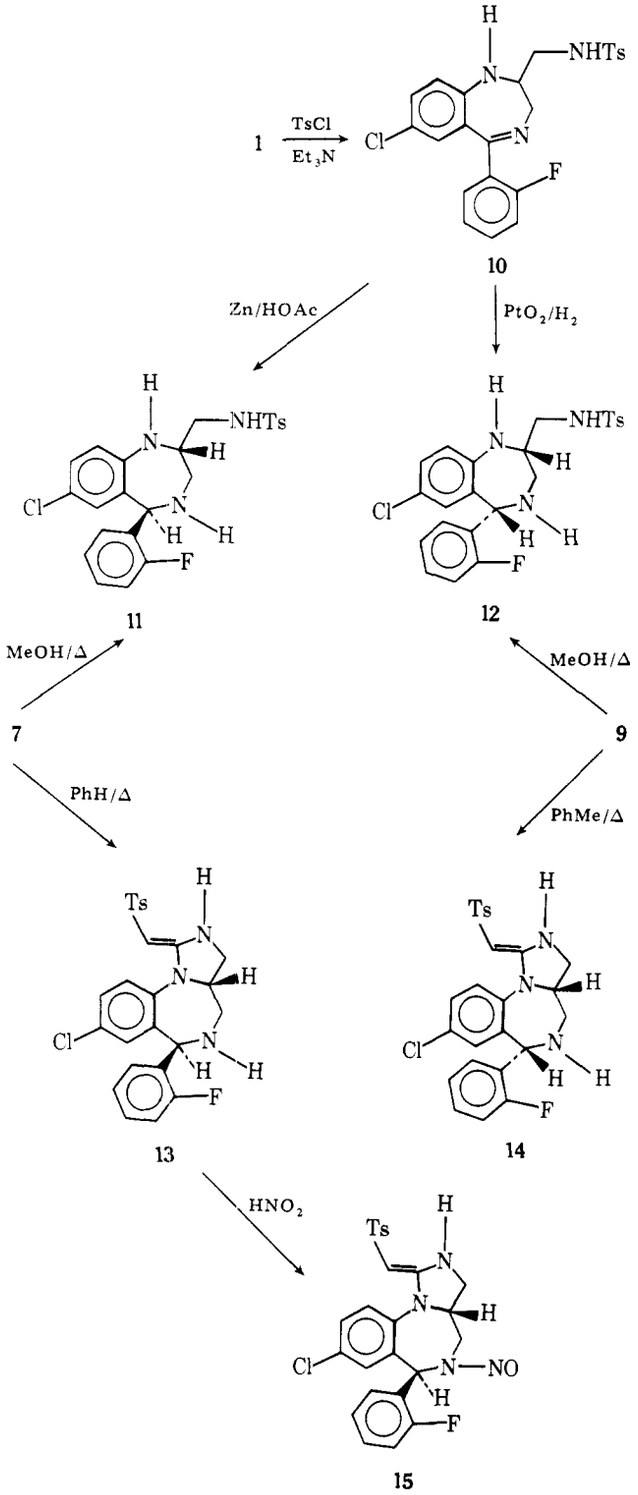
Table I. NMR Spectral Data of Compounds 7 and 9

	7, δ	9, δ		7, J (Hz)	9, J (Hz)
H_a	1.81	0.90	H_aH_b	11	12
H_b	2.28	2.52	H_bH_c	4	4
H_c	3.75	3.73	H_bH_e	2	1
H_d	2.89	2.88	H_cH_e	2	2
H_e	3.54	3.58	H_dH_e	8	8
CH_3	1.56	2.01			

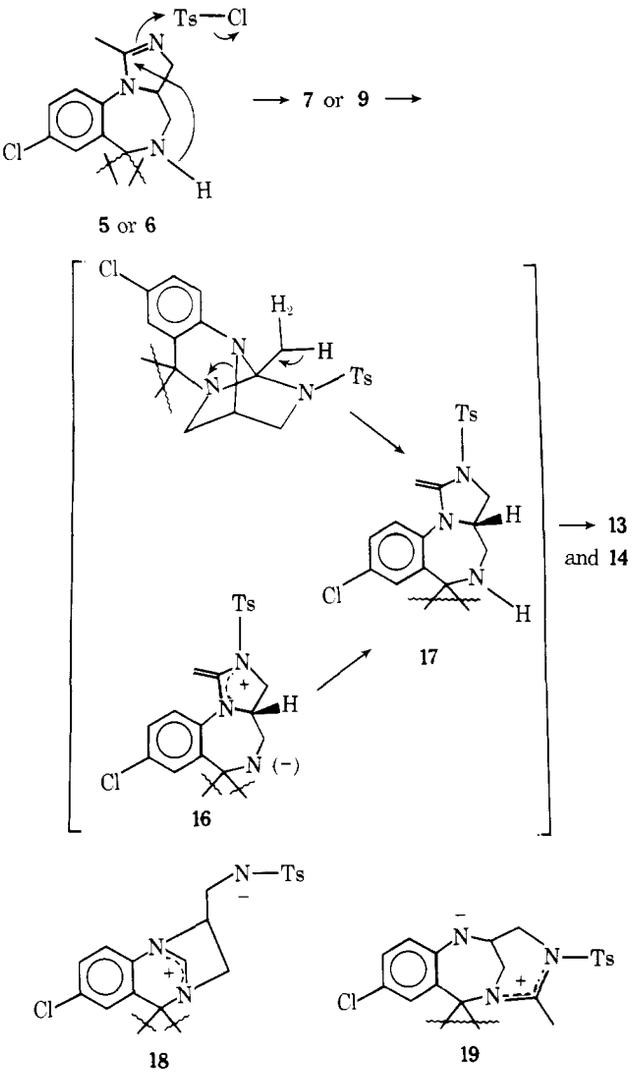
The stereochemical assignments of the fluorophenyl group are consistent with the products obtained by the reduction of the imine bond in **2**. Catalytic hydrogenation delivers hydrogen to the least hindered face of **2**, namely, anti to the imidazoline ring, to give the cis isomer **6**, whereas zinc and acetic acid reduction of **2** gives the trans isomer **5** in which the fluorophenyl group is anti to the imidazoline ring.

Because of the steric environment of the N_5 nitrogen atom in compounds **5** and **6** and also because of the greater basicity of the N_2 nitrogen in the imidazoline ring, tosyl chloride would probably react first at N_2. The formation of compounds **7** and

Scheme II



Scheme III



9 then would most likely occur via intramolecular addition of the N_5 nitrogen to the amidinium ion thus generated.

The tricyclic compounds **7** and **9** were also found to be thermally unstable in aprotic solvents. Refluxing a benzene solution of **7** and a toluene solution of **9** gave the vinyl sulfones **13** and **14**, respectively. Toluene was required for the thermolysis of **9** since we were unable to observe any rearrangement in refluxing benzene. We felt that this is probably due to steric factors. The structures of **13** and **14** were assigned on the basis of X-ray crystallographic analyses of compound **14** and the *N*-nitroso derivative of **13**, compound **15**. The *N*-nitroso derivative **15** was prepared by treatment of **13** with nitrous acid. The use of **15** for the structure determination was necessary since crystals of **13** were opaque.

The unusual transformation of **7** to **13** and **9** to **14** probably proceeds via the aminal **17**, which is formed either by a base-catalyzed ring opening of **7** and **9** or by the zwitterionic intermediate **16** (Scheme III). The specific cleavage of the C_1–N_{12} bond can be explained using the zwitterionic pathway. Cleavage of either the C_1–N_2 bond or the C_1–N_6 bond would lead to zwitterionic intermediates **18** and **19**, respectively, which violate Bredt's rule. A 1,3 migration of the sulfonyl group in the aminal **17** to the terminal methylene group followed by tautomerization leads to the observed vinyl sulfones **13** and **14**.

An analogous rearrangement of a sulfonamide to a sulfone has been reported by both Hellwinkel[5] and Halberkann.[6] The rearrangement of *N*,*N*-diphenyl-*p*-toluenesulfonamide to 2-anilino-4′-methyldiphenyl sulfone proceeds in the presence of an alkyllithium, sulfuric acid, or heat, suggesting an ionic type of rearrangement.

Crystallography. Crystals of **14** and **15** were obtained from ethanol and methylene chloride,[7] respectively. All intensity data were measured on a Hilger Watts diffractometer (Ni-filtered Cu Kα radiation, θ–2θ scans, pulse height discrimination). The crystal data are given in Table II. A multiple solution procedure[8] was used to solve the two structures. Experimental details are summarized in Table III. The fluorophenyl ring in **15** is disordered. The ring exists in one of two

Table II. Summary of Crystal Data for Compounds 14 and 15

	14	15
formula	$C_{25}H_{23}ClFN_3O_2S$	$C_{25}H_{22}ClFN_4O_3 \cdot CH_2Cl_2$[7]
formula wt	483.99	597.92
space group	$P2_1/c$	$P\bar{1}$
a	16.923 (5) Å	9.184 (15) Å
b	10.436 (3) Å	12.374 (15) Å
c	14.534 (7) Å	12.673 (10) Å
α		80.94 (10)°
β	11.70 (3)°	89.93 (15)°
γ		71.90 (12)°
Z	4	2
d_{calcd}	1.347 g/cm^{-3}	1.470 cm^{-3}
μ (Cu Kα)	25.1 cm^{-1}	41.5 cm^{-1}

Table III. Summary of Experimental Details for Crystallographic Analysis of Compounds 14 and 15

	14	15
crystal size	0.35 × 0.33 × 0.04 mm	0.2 × 0.3 × 0.6 mm
maximum θ	48.25°	57°
no. of reflections	1859	3553
absorption correction	yes	no
least-squares refinement	full matrix	block diagonal (six blocks)
heavier atoms	anisotropic	anisotropic
hydrogen atoms	isotropic	isotropic
final R	0.046	0.085
final R_w	0.052	0.105
final difference map largest peak, e Å^{-3}	<±0.2	<±0.3

conformations, related by a 180° rotation about the bond joining the phenyl ring to the imidazobenzodiazepine. The occupancy factors for the two orientations (0.6 for F, 0.4 for F′) were assigned to give approximately equal thermal parameters for the two disordered fluorine atoms.

Experimental Section

Melting points are uncorrected. NMR spectra were recorded on a Varian T-60 or HA-100 instrument and are reported in parts per million from internal tetramethylsilane. Infrared and mass spectra were recorded on Perkin-Elmer 137 and CEC-110B instruments, respectively.

2-Aminomethyl-7-chloro-2,3,4,5-tetrahydro-5-(2-fluorophenyl)-1*H*-1,4-benzodiazepine (4). A mixture of 27.8 g (92 mmol) of 1,[2] 300 mL of acetic acid, and 27.8 g of zinc dust in 450 mL of CH_2Cl_2 was stirred at room temperature for 4 h. The mixture was filtered through Celite, and the filtrate was diluted with ice water, made alkaline with 50% aqueous KOH, and extracted with CH_2Cl_2. The CH_2Cl_2 solution was dried (Na_2SO_4) and concentrated in vacuo. The residue was crystallized from ether and gave 7.6 g (27%) of crude **4**. Recrystallization from ether gave **4** as slightly yellow prisms, mp 127–128 °C.

Anal. Calcd for $C_{16}H_{17}ClFN_3$: C, 62.85; H, 5.61; N, 13.74. Found: C, 62.86; H, 5.61; N, 13.90.

8-Chloro-6-*cis*-(2-fluorophenyl)-3a,4,5,6-tetrahydro-1-methyl-3*H*-imidazo[1,5-*a*][1,4]benzodiazepine (6). A solution of 3.2 g (10 mmol) of **2** in 50 mL of acetic acid and 5 mL of water was hydrogenated at atmospheric pressure in the presence of 0.4 g of prehydrogenated platinum oxide. After 15 min, 225 mL (10 mmol) of hydrogen was absorbed and the catalyst was removed by filtration. The filtrate was concentrated in vacuo and the residue dissolved in CH_2Cl_2. The CH_2Cl_2 solution was washed with aqueous Na_2CO_3, dried (Na_2SO_4), and concentrated in vacuo. The residue was crystallized from ether to give 2.4 g (65%) of crude **6**. Recrystallization from ether gave **6** as colorless prisms: mp 110–112 °C; IR ($CHCl_3$) 1625 cm^{-1} (C=N); NMR (DMF-d_6) δ 2.03 (s, 3, CH_3C=N), 2.5–2.8 (m, 2, C_{2a} H and NH), 3.1–3.4 (m, 2, C_4 H), 3.6–4.1 (m, 2, C_3 H), 5.66 (s, 1, C_6 H), and 6.6–7.5 (m, 7, aromatic H).

Anal. Calcd for $C_{18}H_{17}ClFN_3$: C, 65.55; H, 5.20; N, 12.74. Found: C, 65.83; H, 5.31; N, 12.72.

8-Chloro-6-*trans*-(2-fluorophenyl)-3a,4,5,6-tetrahydro-1-methyl-3*H*-imidazo[1,5-a][1,4]benzodiazepine (5). A. A mixture of 10 g (0.03 mol) of **2**, 10 g (0.15 mol) of zinc dust, 100 mL of acetic acid, and 400 mL of CH_2Cl_2 was stirred at room temperature for 4 h. The zinc salts were removed by filtration through Celite, and the filtrate was diluted with water, neutralized with 50% aqueous KOH, and extracted with CH_2Cl_2. The CH_2Cl_2 solution was dried (Na_2SO_4) and concentrated to dryness in vacuo. The residue was crystallized from ether to give 4.9 g (49%, mp 176–181 °C) of crude **5**. Recrystallization from a mixture of CH_2Cl_2, ether, and petroleum ether gave pure **5**: mp 189–190 °C; IR ($CHCl_3$) 1625 cm^{-1} (–C=N–); NMR ($CDCl_3$) δ 1.90 (br s, 1, NH), 2.03 (s, 3, CH_3), 3.1–4.4 (m, 5, C_3 H, C_{3a} H, and C_4 H), 5.23 (s, 1, C_6 H), 6.60 (brs, 1, aromatic H), and 6.9–7.7 (m, 6, aromatic H).

Anal. Calcd for $C_{18}H_{17}ClFN_3$: C, 65.55; H, 5.20; N, 12.74. Found: C, 65.58; H, 5.08; N, 12.66.

B. A solution of 3 g (10 mmol) of **4** and 10 mL of triethyl orthoacetate in 30 mL of xylene was refluxed for 4 h. The reaction mixture was diluted with ether and extracted with dilute ice-cold HCl. The acid extract was made alkaline with dilute aqueous KOH and extracted with CH_2Cl_2. The CH_2Cl_2 solution was dried (Na_2SO_4) and concentrated to dryness in vacuo. The residue was crystallized from ether to give 2.2 g of **5**. Recrystallization from a mixture of CH_2Cl_2 and ether gave **5** as slightly yellow prisms, mp 189–190 °C.

8-Chloro-6-(2-fluorophenyl)-1-methyl-4*H*-imidazo[1,5-*a*]-[1,4]benzodiazepine (3). A. A mixture of 2.9 g (9 mmol) of **5** and 15 g of activated manganese dioxide in 90 mL of toluene was refluxed for 2 h. The mixture was filtered over Celite and the filtrate concentrated to dryness in vacuo. The residue was crystallized from ether to give 250 mg of **3**, mp 152–153 °C. The product gave no mixture melting point depression with an authentic sample.[2]

B. In a similar manner, **3**, which was prepared from **6**, gave no mixture melting point depression with an authentic sample.

9-Chloro-*endo*-7-(2-fluorophenyl)-1-methyl-2-tosyl-7a,11a-benzo-2,6,12-triazatricyclo[4.4.0.0^{4,12}]decane (7). A solution of 1.6 g (5 mmol) of **5** and 1.3 g (7 mmol) of tosyl chloride in 7.5 mL of CH_2Cl_2 was stirred at room temperature for 90 min, at which time 1.0 mL (7 mmol) of triethylamine was added and stirring was continued for 1 h. The mixture was diluted with 75 mL of ether, and the resulting precipitate was removed by filtration. The filtrate was concentrated to a small volume in vacuo, and 1.6 g (66%, mp 155–158 °C) of crude **7** was collected by filtration. Recrystallization from CH_2Cl_2 gave **7** as colorless needles: mp 160–162 °C; IR 1130 and 1345 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 1.56 (s, 3, CH_3), 1.81 (d, J = 11 Hz, 1, H_a), 2.28 (ddd, J = 2, 4, and 11 Hz, 1, H_b), 2.46 (s, 3, CH_3), 2.87 (d, J = 8 Hz, 1, H_d), 3.54 (ddd, J = 2, 2, and 8 Hz, 1, H_e), 3.75 (dd, J = 2 and 4 Hz, 1, H_c), 4.79 (s, 1, C_7 H), 6.9–7.4 (m, 9, aromatic H), and 7.92 (m, 2, aromatic H); mass spectrum, m/e 483 (M^+).

Anal. Calcd for $C_{25}H_{23}ClFN_3O_2S$: C, 62.04; H, 4.79; N, 8.68. Found: C, 61.82; H, 4.79; N, 8.65.

9-Chloro-*exo*-7-(2-fluorophenyl)-1-methyl-2-tosyl-7a,11a-benzo-2,6,12-triazatricyclo[4.4.0.0^{4,12}]decane (9). A solution of 3.2 g (10 mmol) of **6** and 2.6 g (14 mmol) of tosyl chloride in 150 mL of CH_2Cl_2 was stirred at room temperature. After 1 h, 2 mL (14 mmol) of triethylamine was added and the stirring was continued for 1 h. The mixture was diluted with 150 mL of ether, and the precipitate was removed by filtration. The filtrate was concentrated to a small volume in vacuo, and 3.7 g (76%, mp 164–166 °C) of crude **9** was collected by filtration. Recrystallization from CH_2Cl_2–ether gave **9** as colorless needles: mp 165–167 °C; IR ($CHCl_3$) 1125 and 1380 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 0.90 (d, J = 12 Hz, 1, H_a), 2.01 (s, 3, CH_3–C–N), 2.23 (s, 3, CH_3–C_6H_4), 2.52 (ddd, J = 2, 4, and 12 Hz, 1, H_b), 2.88 (d, J = 8 Hz, 1, H_d), 3.58 (ddd, J = 2, 2, and 8 Hz, 1, H_e), 3.73 (dd, J = 2 and 4 Hz, 1, H_c), 5.78 (brs, 1, C_7 H), 6.9–7.5 (m, 9, aromatic H), and 7.90 (d, J = 8 Hz, 2, aromatic H).

Anal. Calcd for $C_{25}H_{23}ClFN_3O_2S$: C, 62.04; H, 4.79; N, 8.68. Found: C, 61.95; H, 4.79; N, 8.67.

7-Chloro-2,3-dihydro-2-(tosylaminomethyl)-5-(2-fluorophenyl)-1*H*-1,4-benzodiazepine (10). A solution of 3.4 g (11 mmol) of **1** and 2.1 g (11 mmol) of tosyl chloride in 30 mL of pyridine was stirred at room temperature for 2 h. The mixture was concentrated in vacuo, and the residue dissolved in CH_2Cl_2. The solution was washed with water, dried (Na_2SO_4), and concentrated in vacuo to give 4.4 g of a yellow oil. Purification by plug filtration (20 g of SiO_2, ethyl acetate) gave 3.1 g (61%, mp 145–147 °C) of crude **10**. Recrystallization from ether gave **10** as yellow prisms: mp 145–147 °C; IR ($CHCl_3$) 3385 (NH), 1615 (C=N), and 1327 and 1160 (SO_2) cm^{-1}; NMR ($CDCl_3$) δ 2.37 (s, 3, CH_3), 2.96 (brs, 2, SO_2–NH–CH_2), 3.79 (m, 2, C_3 H), 4.06 (m, 1, C_2 H), 4.78 (br d, J = 4 Hz, 1, –NH–), 5.99 (br t, 1, SO_2–NH–), and 6.7–7.7 (m, 11, aromatic H); mass spectrum, m/e 459 (M^+).

Anal. Calcd for $C_{23}H_{21}ClFN_3O_2S$: C, 60.32; H, 4.62; N, 9.18. Found: C, 60.60; H, 4.69; N, 9.19.

7-Chloro-2,3,4,5-tetrahydro-2-(tosylaminomethyl)-5-*trans*-(2-fluorophenyl)-1*H*-1,4-benzodiazepine (11). A. A solution of 1.0 g (2.0 mmol) of **7** in 50 mL of methanol was refluxed for 22 h. The solution was concentrated to dryness in vacuo, and the residue crystallized from a mixture of CH_2Cl_2 and ether to give 0.4 g (40%, mp 168–178 °C) of crude **11**. Recrystallization from methanol gave **11** as colorless needles: mp 180–182 °C; IR ($CHCl_3$) 3350 and 3050 (NH) and 1360 and 1130 (SO_2) cm^{-1}; NMR ($CDCl_3$) δ 2.40 (s, 3, CH_3), 2.8–3.1 (m, 6, C_3 H_2, TsNH–CH_2, and 2-NH), 4.3 (m, 1, C_2 H), 5.13 (s, 1, C_5 H), 5.85 (brs, 1, Ts–NH), and 6.6–7.9 (m, 11, aromatic H).

Anal. Calcd for $C_{23}H_{23}ClFN_3O_2S$: C, 60.06; H, 5.09; N, 9.14. Found: C, 60.26; H, 4.93; N, 9.09.

B. A mixture of 3.0 g (6 mmol) of **10** and 3.0 g (47 mmol) of zinc dust in a mixture of 40 mL of acetic acid and 100 mL of CH_2Cl_2 was stirred at room temperature for 5 h. The excess zinc was removed by filtration through Celite, and the filtrate was made alkaline with 50% aqueous NaOH. The filtrate was diluted with CH_2Cl_2, washed with water, dried (Na_2SO_4), and concentrated in vacuo. The residue crystallized from methanol to give 1.4 g (46%, mp 168–169 °C) of crude **11**. Recrystallization from methanol gave 0.5 g of pure **11**, mp 180–181 °C. A mixture melting point with **11** prepared from orthoamide **7** gave no depression.

7-Chloro-2,3,4,5-tetrahydro-2-(tosylaminomethyl)-5-*cis*-(2-fluorophenyl)-1*H*-1,4-benzodiazepine (12). A. A solution of 1.0 g (2.0 mmol) of **9** in 50 mL of methanol was refluxed for 22 h. The solution was concentrated to a small volume by distillation, and after cooling 0.6 g (65%, mp 192–194 °C) of crude **12** was collected by filtration. Recrystallization from methanol gave **12** as colorless prisms: mp 196–198 °C; IR ($CHCl_3$) 3350 and 3310 (NH), 2680 (NH), and 1314 and 1153 (SO_2) cm^{-1}; NMR ($CDCl_3$) δ 1.8 (brs, 1, NH), 2.42 (s, 3, CH_3), 2.8–3.0 (m, 4, $2CH_2$), 3.2–3.4 (m, 1, C_2 H), 4.8 (br s, 1, NH), 5.26 (s, 1, C_5 H), and 6.5–7.7 (m, 12, aromatic H and NH); mass spectrum, *m/e* 459 (M^+).

Anal. Calcd for $C_{23}H_{23}ClFN_3O_2S$: C, 60.06; H, 5.09; N, 9.14. Found: C, 60.19; H, 4.98; N, 9.18.

B. A mixture of 2.3 g (5 mmol) of **10** and 0.2 g of prehydrogenated platinum oxide in 50 mL of acetic acid was hydrogenated at room temperature and atmospheric pressure until 130 mL of hydrogen was absorbed. The catalyst was removed by filtration and the filtrate concentrated in vacuo to dryness. The residue was dissolved in CH_2Cl_2, washed with aqueous Na_2CO_3, dried (Na_2SO_4), and concentrated in vacuo to dryness. The residue crystallized from methanol to give 1.4 g (60%, mp 192–195 °C) of crude **12**. A mixture melting point with **12** prepared from **9** gave no depression.

8-Chloro-*trans*-6-(2-fluorophenyl)-1-([(4-methylphenyl)sulfonyl]methylene)-2,3,3a,4,5,6-hexahydro-1*H*-imidazo[1,5-a][1,4]benzodiazepine (13). A solution of 2.8 g (6 mmol) of **7** in 100 mL of dry benzene was refluxed for 1.5 h. The reaction mixture was concentrated in vacuo to dryness. The residue was crystallized from THF to give 2.4 g (85%, mp 244–246 °C) of crude **13**. Recrystallization from THF gave pure **13** as colorless needles: mp 244–245 °C; IR ($CHCl_3$) 3420 (NH) and 1328 and 1166 (SO_2) cm^{-1}; NMR ($CDCl_3$–Me_2SO-d_6) δ 2.43 (s, 3, CH_3), 2.0–4.4 (m, 7, C_3 H_2, C_{3a} H, C_4 H_2, NH, and =CH), 5.15 (s, 1, C_6 H), 6.56 (s, 1, C_6 H), and 7.1–7.9 (m, 11, aromatic H and NH); mass spectrum, *m/e* 483 (M^+).

Anal. Calcd for $C_{25}H_{23}ClFN_3O_2S$: C, 62.04; H, 4.79; N, 8.18. Found: C, 61.77; H, 5.01; N, 8.47.

8-Chloro-*cis*-6-(2-fluorophenyl)-1-([(4-methylphenyl)sulfonyl]methylene)-2,3,3a,4,5,6-hexahydro-1*H*-imidazo[1,5-a][1,4]benzodiazepine (14). A stirred suspension of 5 g (10 mmol) of **9** in 300 mL of dry toluene was refluxed for 7 h. A small amount of insoluble precipitate was separated by filtration. The filtrate was concentrated in vacuo to dryness, and the residue crystallized from a mixture of CH_2Cl_2 and ether to give 3.4 g (70%, mp 116–118 °C) of crude **14**. Recrystallization from ethanol gave pure **14** as colorless prisms: mp 186–188 °C; IR ($CHCl_3$) 3405 (NH) and 1130 (SO_2) cm^{-1}; NMR ($CDCl_3$) δ 2.4 (brs, 1, NH), 2.43 (s, 3, CH_3), 2.80 (br d, 2, C_3 H_2), 3.17 (m, 1, C_4 H), 3.7–4.2 (m, 2, C_4 H and C_{3a} H), 4.32 (s, 1, =CH), 5.48 (s, 1, C_6 H), and 6.2–7.8 (m, 12, aromatic H and NH); mass spectrum, *m/e* 483 (M^+).

Anal. Calcd for $C_{25}H_{23}ClFN_3O_2S$: C, 62.04; H, 4.79; N, 8.68. Found: C, 62.32; H, 4.95; N, 8.90.

8-Chloro-6-(2-fluorophenyl)-5-nitroso-1-([(4-methylphenyl)sulfonyl]methylene)-2,3,3a,4,5,6-hexahydro-1*H*-imidazo[1,5-a][1,4]benzodiazepine (15). A mixture of 1 g (2 mmol) of **13**, 0.2 g (3 mmol) of sodium nitrite, and 15 mL of acetic acid was stirred at room temperature for 1 h. The mixture was poured over ice, made alkaline with NH_4OH, and extracted with a mixture of CH_2Cl_2 and THF. The organic layer was dried (Na_2SO_4) and concentrated to dryness in vacuo. The residue crystallized from a mixture of CH_2Cl_2 and THF to give 0.4 g (35%, mp 211–212 °C) of crude **15**. Recrystallization from a mixture of CH_2Cl_2 and ether gave **15** as pink prisms: mp 213–214 °C; IR ($CHCl_3$) 3410 (NH) and 1610 and 1595 (N=O, SC=C); NMR ($CDCl_3$–Me_2SO-d_6) δ 2.42 (s, 3, CH_3), 3.4–4.5 (m, 5, C_3 H, C_4 H, and C_{3a} H), 4.8–5.0 (m, 1, C_6 H), 6.4–6.6 (m, 1, aromatic H), and 6.8–7.7 (m, 10, aromatic H); mass spectrum, *m/e* 512 (M^+).

Anal. Calcd for $C_{25}H_{22}ClFN_4O_3S$: C, 58.53; H, 4.32; N, 10.92. Found: C, 58.70; H, 4.35; N, 11.15.

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Supplementary Material Available: Tables IV and V, the bond lengths and angles in compound **14**, Tables VIII and IX, the final atomic parameters for **14**, Tables VI and VII, the bond lengths and bond angles in **15**, and Tables X and XI, the final atomic parameters for **15** (9 pages). Ordering information is given on any current masthead page.

References and Notes

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